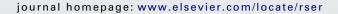
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A review on adsorption cooling systems with adsorbent carbon

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ABSTRACT

This study introduces a review for the potential cooling systems which uses carbon materials as an adsorbent. Also, the adsorption carbon pairs (pairs where the carbon is the adsorbent) which is still under researches were reviewed. The maximum COP (coefficient of performance) of the cooling systems was 0.8 for activated carbon/ethanol pair. The study concluded that the performances of the potential adsorption cooling systems using carbon are still not satisfied. It was concluded that there is an opportunity for the adsorption carbon pairs to introduce a new cooling system with a promising performances.

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1. Introduction

Adsorption cooling systems have received a lot of attention due to their effective cold production based on waste heat or solar energy utilization. Adsorption cooling systems are environmentally friendly and they can utilize the low-grade waste heat or renewable energy as the main driving energy and thus have a large energy saving potential.

The basic adsorption cooling system consists of two linked vessels, one of which contains the adsorbent–refrigerant pair (generator) and the second which contains only refrigerant (evaporator-condenser). Both vessels are initially at low pressure and temperature with a high refrigerant concentration within the adsorbent and only refrigerant gas in the second vessel as shown in Fig. 1. The first step is heating up the generator so the refrigerant gas is driven out from the adsorbent while the pressure of the full system rises (desorption) (a). The desorbed gas is condensed in the evaporator-condenser by rejecting heat (b). When the generator has reached the desirable refrigerant concentration (c), it is then cooled to its initial temperature and re-adsorbs the refrigerant, reducing the

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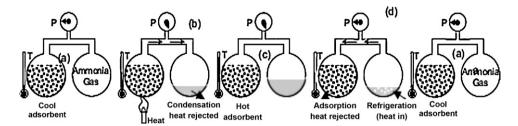


Fig. 1. Principale of adsorption cooling system.

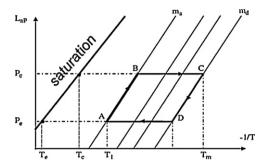


Fig. 2. The ideal of adsorption cooling in clapeyron diagram.

pressure (adsorption). The lower pressure causes the refrigerant liquid contained in the evaporator condenser to boil, absorbing heat and therefore producing the necessary cooling effect (d) [1].

The basic adsorption cycle for cooling consists of four processes represented in Fig. 2. Process A–B is an isosteric heating process where, process B–C is an isobaric heating process. Cooling of the adsorbent provokes a drop of pressure as clear in process C–D. Meanwhile, the liquid refrigerant is transferred into the evaporator the adsorbent continues to decrease in temperature and pumps the liquid refrigerant, which evaporates and extracts heat from the evaporator in process D–A generating a cooling effect [2].

Adsorption pair means the pair which consists of adsorbent and refrigerant. The adsorption working pair is the vital part in the adsorption refrigeration cycle. The selection of any pair of adsorbent-adsorbate for refrigeration applications depends on certain desirable characteristics of their constituents. These characteristics range from their thermodynamic and chemical properties to their physical properties and even to their costs or availability.

The adsorbate or refrigerant should have the following properties [3,4]:

- 1. Evaporation temperature below 0 °C.
- Small molecular size to enable it to be adsorbed into the adsorbent.
- 3. High latent heat of vaporization and low specific volume.
- 4. Thermally stable with the adsorbent at the cycle operating temperature ranges.
- 5. Non-toxic, non-corrosive and non-flammable.
- 6. Low saturation pressures (above atmospheric) at normal operating temperature.

The important considerations influencing the choice of a suitable adsorbent are [3,4]:

- 1. Adsorption of large amount of the adsorbate under low temperature conditions.
- 2. Desorption of most of the adsorbate when exposed to thermal energy.
- 3. Possession of high latent heat of adsorption compared to sensible heat.
- 4. No deterioration with age or use.

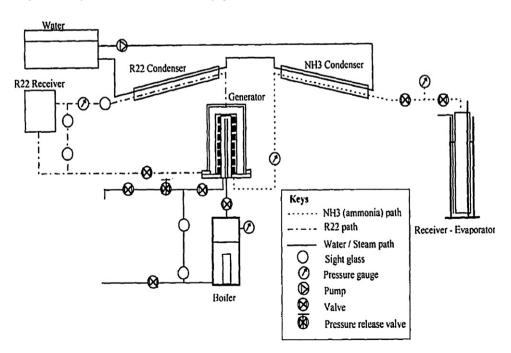


Fig. 3. Layout of adsorption refrigerator with monolithic carbon/ammonia pair.

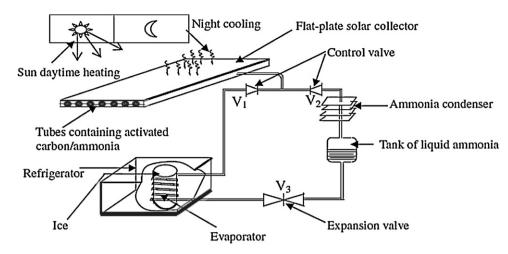


Fig. 4. Schematic of solar finned tube system.

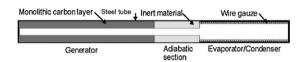


Fig. 5. A single module of the multiple bed adsorption system.

- 5. Non-toxic and non-corrosive.
- 6. Low cost and widely available.

The study will introduce a review for the already applied adsorption cooling systems using carbon materials as an adsorbent. The study will focus on the performance of these systems to obtain the characteristics of each system. The design of each system will be introduced in a brief. The study will also introduce a review for new adsorption pairs which contain carbon as an adsorbent. The information about the new pairs will concentrate on driving temperature, adsorption capacity, evaporation temperature and heat of adsorption.

2. Adsorption cooling systems

2.1. Activated carbon/ammonia

Activated carbon is the common term used for a group of adsorbing substances of crystalline form, having large internal pore

structures that make the carbon more adsorbent. Activated carbon is manufactured according to the Ostreijkos patents of 1900 and 1902. Activation basically means that pores are created in a non-porous material by means of chemical reactions. There are two different methods for this, chemical activation and activation by steam.

Activated carbons are made by pyrolizing and carbonizing source materials, such as coal, lignite, wood, nut shells and synthetic polymers, at high temperatures (700–800 °C). Activated carbons are available in many forms including powders, microporous, granulated, molecular sieves and carbon fibers [5].

Tamainot-Telto and Critoph [6] presented a laboratory prototype of an adsorption cooling machine which uses an activated monolithic carbon/ammonia pair. A layout of the experimental rig is shown in Fig. 3. The generator was made of aluminum with a hollowed inner shell and two outer vessels. The outside surface of the inner shell had fins and 15 monolithic carbon discs. The fins have slots to allow the distribution of ammonia between all the carbon discs in the generator. The generator was heated to 250 °C. The total mass of the carbon was estimated to be about 800 g. In the heating phase the carbon was heated by steam supplied to the center hollow, while in the cooling phase the carbon was cooled by boiling refrigerant R22 in the outer shell. An electrical heating coil, which was inserted at the base of the boiler, can produce steam ranging from 100 °C to 150 °C. The heating power

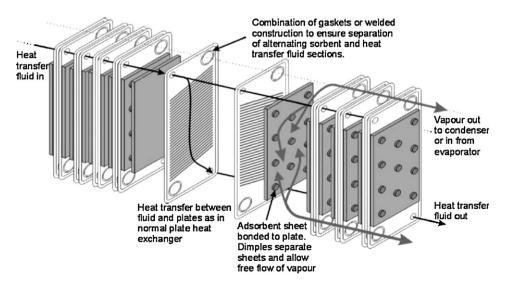


Fig. 6. Schematic of a plate-type sorption generator.

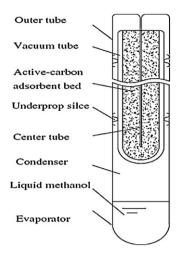


Fig. 7. Sketch of the freeze proof solar cooling tube.

was controlled by a variable supply unit and its maximum value was 2 kW. The cooling water was stored in a tank. The receiver-evaporator was a vessel of 300 ml capacity and was made from stainless steel. After the heating phase the receiver was inserted inside an ice bucket which contains water and which was well insulated.

The experimental results demonstrated that the maximum SCP (specific cooling power) and COP (coefficient of performance) were $60\,\mathrm{W/kg_{carbon}}$ and 0.12, respectively. The evaporating and condensing temperature ranges were $-20\,^{\circ}\mathrm{C}$ to $0\,^{\circ}\mathrm{C}$ and $20\,^{\circ}\mathrm{C}$ to $45\,^{\circ}\mathrm{C}$, respectively. Simulation results with a conventional carbon ammonia pair gave an estimate of about $1600\,\mathrm{s}$ for the cycling time of the system.

Al Mers et al. [7] and Louajari et al. [8] studied the optimal design of cylindrical finned reactor for solar adsorption cooling machine working with activated carbon/ammonia pair. The studies presented a model describing heat and mass transfer in a cylindrical finned reactor of solar adsorption refrigerator. The validity of the model had been tested by using experimental results. The solar reactor studied is represented in Fig. 4 it was constituted of a transparent cover, a lateral and rear insulation and a steel adsorber containing the activated carbon. The optimization results showed

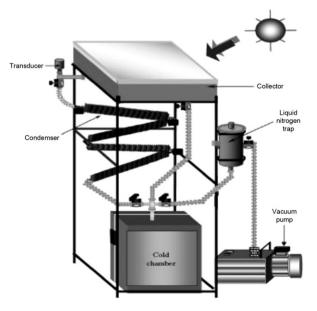


Fig. 8. Layout of the experimental solar adsorption refrigeration.

that when the number of fins varies between 5 and 6 the COP be about 0.106 at 0 $^{\circ}$ C evaporator temperature. The adsorption temperature was 97 $^{\circ}$ C.

Critoph [9] studied a multiple bed regenerative adsorption cycle using the monolithic carbon/ammonia pair. A single module is shown in Fig. 5 where, the complete system, consisting of 32 modules had been modeled. The system was found to reach a COP of 0.85 with a cooling power of 400 W.

Tamainot-Telto et al. [1] investigated the carbon–ammonia pairs for adsorption refrigeration applications. A thermodynamic cycle model was used to select an optimum adsorbent–refrigerant pair that according to the cooling production, the heating production, or the COP. The model was based mainly on the adsorption equilibrium equations of the adsorbent–refrigerant pair and heat flows. The simulation results of 26 various activated carbon–ammonia pairs for three cycles (single bed, two-bed and infinite number of beds) were presented at typical conditions for ice making, air conditioning and heat pumping applications. The driving temperature varied from 80 °C to 200 °C. The carbon absorbents investigated were mainly coconut shell and coal based types in multiple forms: monolithic, granular, compacted granular, fiber, compacted fiber, cloth, compacted cloth and powder.

Considering a two-bed cycle, the best thermal performances based on power density were obtained with the monolithic carbon KOH-AC. At a driving temperature of $100\,^{\circ}$ C; the cooling production was about $66\,\mathrm{MJ/m^3}$ with 0.45 COP and $151\,\mathrm{MJ/m^3}$ with 0.61 COP for ice making and air conditioning, respectively. The heating production was about $236\,\mathrm{MJ/m^3}$ with 1.5 COP.

Critoph and Metcalf [10] studied the specific cooling power intensification limits in carbon/ammonia adsorption refrigeration systems. A model for a sorption refrigeration system using monolithic carbon and ammonia was used. The system was based on a plate-type sorption generator which is shown in Fig. 6.

The system was simulated in a finite-difference model. It should be possible to construct a monolithic carbon/ammonia refrigeration system utilizing a simple non-regenerative cycle with a COP typically about 0.3 and $2\,\mathrm{kW/kg}$ SCP. The design was based on a 2 mm thick carbon layer with 0.2 mm stainless steel plates and 0.5 mm thick fluid channels. The driving and evaporation temperatures were 200 °C and 15 °C, respectively, where the minimum cycle time was 12 s.

2.2. Activated carbon/methanol

Activated carbon and methanol is one of the most common working pairs due to the large adsorption quantity and lower adsorption heat, which is about $1800-2000\,kJ/kg$. However, activated carbon/methanol has the disadvantage of operating under sub-atmospheric pressure [5]. The maximum adsorption quantity in activated carbon is 0.45 g/g and the latent heat at $-30\,^{\circ}\text{C}$ is about $1229.1\,kJ/kg\,^{\circ}\text{C}$ [11]. However, the methanol decomposes at $120\,^{\circ}\text{C}$ through either a dehydrogenation or a dehydration mechanism to form formaldehyde (HCHO) or dimethyl ether (CH₃OCH₃) [12]. The aluminum alloy was found to have a stronger catalytic effect on the decomposition reaction than copper [12].

Zhao et al. [13] introduced a mechanical and experimental study on freeze proof solar powered adsorption cooling tube using active carbon/methanol working pair. Fig. 7 shows, the freeze proof solar cooling tube. The outer tube, center tube and vacuum tube were made of hard borosilicate glass. The diameter of the outer tube was 58 mm, and the diameters of the vacuum tube were 47 mm and 37 mm. The diameter for the center tube was 10 mm.

It was found that where the maximum adsorbent bed temperature was $110\,^{\circ}$ C, the evaporation temperature was about $-4\,^{\circ}$ C. The cooling capacity of the freeze proof solar cooling tube was about $87-99\,\text{k}$; and the COP was about 0.11.

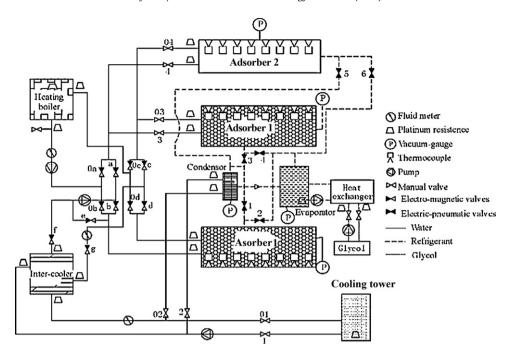


Fig. 9. Schematics of adsorption system.

Lemmini and Errougani [14] studied the experimentation of solar adsorption refrigeration. The used system is shown in Fig. 8. The refrigerant was methanol, and the adsorbent was a micro porous activated carbon (AC35). The collector was made from copper plates 1.2 mm thick, wais a parallelepiped with sides of 85 mm and a width of 60 mm. It contains 14.5 kg of AC35, which were spread between 13 fins, 850 mm long and 5 mm large. A stainless steel grid was used in order to create a free space of 1 mm between the rear plate of the collector and the activated carbon, for the transit of refrigerant vapor during desorption. In order to improve the solar absorption of the collector, the front face was painted with a selective coating and glazed with a transparent cover. The solar COP (cooling energy/solar energy) ranges between 5% and 8% for an irradiation between 12,000 and 28,000 kJ/m².

Wang et al. [15] studied the performance of activated carbon/methanol adsorption systems concerning heat and mass transfer. Three types of adsorbers were discussed. The size of cylindrical adsorber1 was 0325×1400 mm, while adsorber2 and adsorber3 were rectangular with the size as $286 \times 210 \times 2100$ mm, and $387 \times 422 \times 1539$ mm, respectively. Fig. 9 shows a schematic for the system. The adsorption system was consisted of three adsorbers, one condenser, and one evaporator. Glycol was used as the cooling medium to take the cooling effect outside from the evaporator. Experiments with heat and mass recovery showed that the

performance of adsorber3 was much better than that of adsorber1 and adsorpber2. This was because the mass transfer channels of adsorber3 were more reasonably arranged than that of adsorber2 and adsorber1. COP and SCP of adsorber3 were respectively about 0.125 and $16\,\mathrm{W/kg}$ when the cycle time was $56\,\mathrm{min}$ and the desorption temperature was $120\,^{\circ}\mathrm{C}$.

El-Sharkawy et al. [16] studied the adsorption of methanol onto carbon based adsorbents. The study presented the isothermal characteristics of methanol adsorption onto two specimens of activated carbons namely Maxsorb III and Tsurumi activated charcoal. Fig. 10 shows the schematic layout of the experimental apparatus. The evaporator was consisted of a stainless steel tube of 20 mm inner diameter connected with a glass tube of 4.8 mm inner diameter. The adsorber chamber was made from stainless steel with 120 mm outer diameter and 90 mm height supported with circular fins at its inner base. Employing a time-independent mathematical model, the pairs had been studied and compared with that of three other types of carbon based pairs.

For the evaporator temperature of $15\,^{\circ}$ C, the Maxsorb III can adsorb methanol of $1.2\,g/g$ within about $160\,\text{min}$. The change of SCP and COP with regeneration temperatures for Maxsorb III/methanol, activated charcoal/methanol, LH/methanol, DEG/methanol and AC-35/methanol pairs was studied. The maximum COP was $0.78\,$ with Maxsorb III/methanol at regeneration temperature of $90\,^{\circ}$ C.

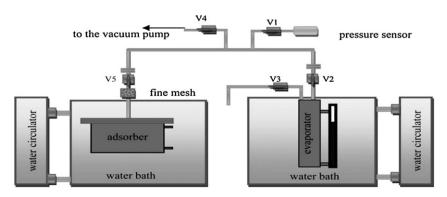


Fig. 10. Schematic layout of the experimental set-up.

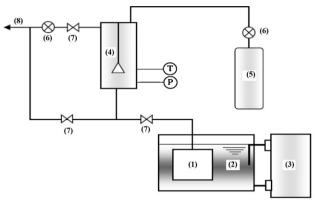
Theoretical results showed that the superiority of Maxsorb III/methanol pair among other carbonaceous pairs for both of air conditioning and ice-making applications.

2.3. Activated carbon/ethanol

The performance of refrigeration system using activated carbon and ethanol was studied by many researchers. Using Maxsorb III as an activated carbon El-sharkawy et al. [17] introduced a solar powered adsorption cooling system. The system had been experimentally investigated using a thermo gravimetric analyzer (TGA) unit over adsorption temperatures ranging from 20 to 60 °C. The system is shown in Fig. 11.

The adsorbent sample was $89.3\,\mathrm{mg}$ and the evaporator temperature was $15\,^\circ\mathrm{C}$. The sample was regenerated at $120\,^\circ\mathrm{C}$ under vacuum conditions for several hours. The weight of the adsorbent sample was logged within a time interval of $0.5-1\,\mathrm{s}$. The adsorption capacity of Maxsorb III of ethanol was estimated experimentally to be $1.2\,\mathrm{g/g}$ with $80\,^\circ\mathrm{C}$ driving temperature. The COP of the system was about 0.8 at evaporation temperature of $15\,^\circ\mathrm{C}$. The specific cooling effect was about $420\,\mathrm{kJ/kg}$ at an evaporator temperature of $7\,^\circ\mathrm{C}$.

A two bed adsorption cooling system using activated carbon fibers (ACF)/ethanol as an adsorption pair was introduced by Saha et al. [18–20]. The system is shown in Fig. 12. The chiller was operational with a 30 °C heat source and heat sink temperature difference. With a cooling water temperature at 30 °C, optimum COP values were obtained with driving source temperatures between 85 and 95 °C. Optimum cooling capacity values were obtained for a cycle time at 600 s with a fixed pre-heating or pre-cooling cycle time. Optimum switching time for the chiller was obtained



(1)Evaporator; (2)Constant temperature water bath; (3)Water circulator; (4)TGA reacting chamber; (5)Helium cylinder; (6)Pressure regulator; (7)Valve; (8)To the vacuum pump.

Fig. 11. Schematic diagram of the set-up.

between 30 and $50\,\mathrm{s}$. The COP reached to about 0.6 with a cycle time of $600\text{--}700\,\mathrm{s}$.

3. New carbon adsorption pairs

3.1. Activated carbon/hydrogen

The characteristics of hydrogen adsorption on activated carbon were experimentally studied by Huang et al. [21] and Yoshitsugu et al. [22]. Various carbon materials were obtained in the study. Nano particles of palladium were impregnated in the prepared

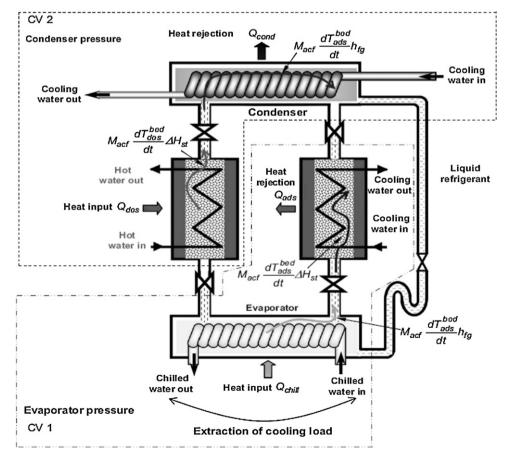


Fig. 12. Schematic of the two-bed ACF ethanol adsorption system.

Table 1Outline of adsorption cooling systems which uses carbon as adsorbent material.

Adsorption pair			COP	$T_{\rm e}$ (°C)	$T_{\rm d}$ (°C)	SCP (W/kg)
Carbon/ammonia	Activated carbon	[6]	0.12	-20	100-150	60
		[7,8]	0.106	0	97	N.A
	Carbon	[9]	0.2-0.5	-25	100	600
		[10]	0.3	15	200	2000
	Activated carbon/methanol	[13]	0.11	-4	110	N.A
		[14]	0.05-0.08	N.A	N.A	N.A
		[15]	0.125	N.A	120	16
		[16]	0.78	15	90	N.A
Carbon/ethanol	Activated carbon/ethanol	[17]	0.8	15	80	N.A
,	Activated carbon fibers/ethanol	[18,19]	0.6	30	85-95	N.A

activated carbon. The maximum hydrogen adsorption capacity was $0.0289\,\mathrm{g/g}$ at $-196\,^\circ\mathrm{C}$ under $0.1\,\mathrm{MPa}$. With 10% palladium the adsorbent capacity of hydrogen could be reached to $0.055\,\mathrm{g/g}$ under a pressure up to $6\,\mathrm{MPa}$ at $30\,^\circ\mathrm{C}$. The isosteric heat was in a range of $5.6-7.9\,\mathrm{kJ/mol}$ for the pair at -196 to $-183\,^\circ\mathrm{C}$.

Jin et al. [23] studied the hydrogen adsorption characteristics of activated carbon based on coconut-shell. The maximum hydrogen adsorption capacity of 0.85 wt.% at 100 bars, 25 °C was obtained. Hydrogen adsorption in carbon nanostructures was investigated by Poirier et al. [24]. Excess adsorption capacity was evaluated at equilibrium pressures and temperatures ranging from 0.1 to 10.5 MPa and –196 to 22 °C, respectively. It was found that at room temperature, carbon nanofibers can adsorb up to 0.7 wt.% at 10.5 MPa.

Henneberg et al. [25] introduced thermo-analytical investigations of hydrogen adsorption on carbon materials. Measurements were at temperatures between -10 and $25\,^{\circ}\text{C}$ and pressures up to 140 bar. All investigated carbon nanofibers shown a hydrogen uptake below 0.3 wt.%.

3.2. Activated carbon/nitrogen

A pair of iodine doped activated carbon fibers/nitrogen was studied by Yang and Kaneko [26] to estimate its adsorption characteristics. The adsorption capacity of nitrogen was found to be about $0.75~\rm g/g$ at $-196~\rm ^{\circ}C$. The isosteric heat was to be about $11.7~\rm kJ/mol$. Activated carbon fibers without iodine was also studied with nitrogen as an adsorption pair. The results for activated carbon fibers without iodine showed the same amount of isosteric heat and more adsorption capacity than that for activated carbon fibers with iodine $(0.8~\rm g/g)$.

The adsorption characteristics of beads activated carbon as an adsorbent and nitrogen as an adsorbate were introduced by Shen et al. [27]. Adsorption equilibrium for nitrogen was measured at different temperatures and pressures. The highest adsorption capacity was $0.00756\,\mathrm{g/g}$ at $30\,^\circ\mathrm{C}$ adsorption temperature and $100\,\mathrm{kPa}$ adsorption pressure. The isosteric heat magnitude was also determined to be $17.5\,\mathrm{kJ/mol}$.

3.3. Activated carbon/diethyl ether

Granular activated carbon and diethyl ether was introduced as an adsorption pair by Al-Ghoutia et al. [28]. The normal boiling temperature of diethyl ether ($(C_2H_5)_2O$) is 34.45 °C. The isosteric heat of the pair was found to be 45.84 kJ/mol and the time of equilibrium adsorption was ranged from 45 to 20 min as adsorption temperature was varied from 26 to 50 °C. Experimentally the adsorption capacity of the diethyl ether on activated carbon at 26, 35, and 50 °C were 1.18, 1.63, and 1.39 mg/g, respectively at 10 kPa.

3.4. Activated carbon/R134a

The adsorption characteristics of activated carbon and R134a (1,1,1,2-tetrafluoroethane $C_2H_2F_4$) had been widely researched theoretically and experimentally by many researchers [29,30]. Using Maxsorb III as an adsorbent, the minimum isosteric heat for the pair was estimated to be about 21 kJ/mol. The maximum capacity for activated carbon of R134a was 2 g/g at 30 °C isotherms adsorption at a pressure of 800 kPa. At 25 °C the time of adsorption was estimated to be 1200 s. The normal boiling temperature of R134a is -26.55 °C and the molecular weight is 102.03.

3.5. Activated carbon/R507A

Maxsorb III/R507A (1,1,1-trifluoroethane $C_2H_3F_3$) was used as an adsorption pair. The R507a is R125 and R134a in a fraction weight of 50% to 50% and its normal boiling point is $-47.1\,^{\circ}$ C. When the isotherms adsorption temperature was 20 °C, the Maxsorb III can adsorb R507A as high as 1.3 g/g within an adsorption time interval of 1100 s [30].

3.6. Activated carbon/n-butane

The adsorption isotherms of n-butane (C_4H_{10}) on pitch based activated carbon (Maxsorb III) at temperatures ranging from 25 °C to 55 °C and at different equilibrium pressures between 20 and 300 kPa have been experimentally measured. The isosteric heat of n-butane on Maxsorb III was $406 \, \text{kJ/kg}$ with a loading of 0.7 g/g. The derived monolayer capacity of Maxsorb III–n-butane pair had been measured as 0.8 g/g with an adsorption temperature of 35 °C and 232.34 kPa. The time of adsorption at 25 °C was about 1400 s [31].

Table 2Adsorption characteristics of the new carbon adsorption pair.

Adsorption pair	C (kg/kg)	$T_{\rm ads}$ (°C)	$q_{\rm st}$ (kJ/kg)	P (bar)
Activated carbon/hydrogen [21,22]	0.055	30	2800-3950	6
Activated carbon fibers/nitrogen [26]	0.75	-4	418	N.A
Activated carbon/diethyl ether [28]	0.00139	50	619	0.1
Activated carbon/R134a [29]	2	30	210	8
Activated carbon/R507a [30]	1.3	20	N.A	N.A
Activated carbon/n-butane [31]	0.8	35	406	2.3
Activated carbon/CO ₂ [27]	0.084	30	680	1

3.7. Activated carbon/CO₂

An activated carbon in beads form used with CO_2 as an adsorption pair to study experimentally its adsorption equilibria and kinetics. Adsorption equilibrium for CO_2 was measured at different temperatures and pressures. The highest adsorption capacity was $0.0844 \, g/g$ at $30 \, ^{\circ}C$ and $100 \, kPa$. The isosteric heat was determined to be $23.17 \, k/mol \, [27]$.

4. Summery

Table 1 summarizes the performances of the potential adsorption cooling systems which uses carbon as an adsorbent. It is clear from the table that, the system with activated carbon ethanol pair has the highest COP value. This system has the advantage of a relatively low driving temperature. The system has the disadvantage of a relatively high evaporation temperature about because of its boiling temperature is about 78 °C.

Table 2 contains the summery of the adsorption characteristics of the new adsorption pairs which use carbon as an adsorbent material. The table introduces the adsorption capacity, adsorption temperature, isosteric heat and pressure. It is clear from the table that the activated carbon/R134a pair has the highest adsorption capacity and the minimum value of the isosteric heat.

5. Conclusion

The study reviewed the adsorption pairs which using carbon as an adsorbent in cooling applications. A lot of materials were used with carbon as a refrigerant in the adsorption pairs. Some of these pairs were used to built cooling systems and some of it is still under researches. The highest values of COP were achieved by the systems which used methanol and ethanol as a refrigerant where it was 0.78 and 0.8, respectively. Many of the new pairs showed a promising future for cooling application. Finally it is clear from the study that the adsorption cooling is still need for more attention and is still have the opportunity to be a traditional device.

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